Comment on “Theoretical investigations of the hyperfine interactions for Co$^{2+}$ in the fluoroperovskites” [Chem. Phys. 348 (2008) 199]

A. Trueba, J.M. García-Lastra, M.T. Barriuso, J.A. Aramburu, M. Moreno

A. Trueba a, J.M. García-Lastra b, M.T. Barriuso c, J.A. Aramburu a,*, M. Moreno a

a Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Universidad de Cantabria, Avda. de los Castros s/n, 39005 Santander, Spain
b Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco, 20018 San Sebastián, Spain
c Departamento de Física Moderna, Universidad de Cantabria, Avda. de los Castros s/n, 39005 Santander, Spain

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In a recent study Wu et al. have reported a theoretical study of spin Hamiltonian parameters measured for substitutional Co$^{2+}$ impurities in three host lattices with the normal perovskite structure (K MgF$_3$, K ZnF$_3$ and CsCdF$_3$) and also in LiBaF$_3$ (displaying an inverted perovskite structure) where Co$^{2+}$ enters the Li$^+$ site. In their analysis the authors assume that the spin Hamiltonian parameters can be explained through the isolated octahedral CoF$_6^{2-}$ complex formed in all cases by the impurity and the six nearest F$^-$ ions. In this comment, we show that the anomalous changes experienced by magnetic and optical parameters on passing from K MgF$_3$:Mn$^{2+}$ to BaLiF$_3$:Mn$^{2+}$ (M = Ni, Mn, Co) all obey to the same cause: the different shape of the electrostatic potential due to all ions lying outside of the CoF$_6^{2-}$ complex in the normal and inverted perovskite structures.

Abstract

In a recent study Wu et al. have reported a theoretical study of spin Hamiltonian parameters measured for substitutional Co$^{2+}$ impurities in three host lattices with the normal perovskite structure (K MgF$_3$, K ZnF$_3$ and CsCdF$_3$) and also in LiBaF$_3$ (displaying an inverted perovskite structure) where Co$^{2+}$ enters the Li$^+$ site. In their analysis the authors assume that the spin Hamiltonian parameters can be explained through the isolated octahedral CoF$_6^{2-}$ complex formed in all cases by the impurity and the six nearest F$^-$ ions. As to the method of analysis, the authors do not use theoretical calculations for deriving from them the spin Hamiltonian parameters measured experimentally. What they do is to fit both experimental gyromagnetic factor, g, and hyperfine constant, A, to some approximate expressions where covalency has partially been taken into account. An average covalency and also 10Dq crystal-field splitting parameter are both derived from experimental optical transitions. Moreover, in that analysis several drastic approximations are used in such a way that g factor and the hyperfine constant are written in terms of only one fitting parameter. The latter quantity is determined searching the closest agreement with the experimental g and A values. Such assumptions lead, for instance, to $f_{\sigma} - f_{p} = -0.1\%$ for CsCdF$_3$:Co$^{2+}$ thus implying that $\sigma$ covalency in the antibonding $e_g$ level is surprisingly smaller than that for the $t_{2g}$ orbital where bonding has only a $\pi$ character. This conclusion is against the figure $f_{\sigma} - f_{p} = 4\%$ derived by Ziaei [2] from ENDOR measurements on CsCdF$_3$:Co$^{2+}$. Along this line the values $f_{p} = 6.8 \pm 0.6\%$ and $f_{p} = 1 \pm 0.4\%$ have been measured for MgO:Fe$^{3+}$ while for MgO:Mn$^{2+}$ the obtained figures are $f_{p} = 1.4 \pm 0.6\%$ and $f_{p} = 0.6 \pm 0.4\%$ [3]. Similarly, the ratio $f_{\sigma}/f_{p}$ has been calculated to be close to 2 for both KMgF$_3$:Mn$^{2+}$ and LiBaF$_3$:Mn$^{2+}$ [4]. Despite this fact, it is however not surprising that the theoretical $g$ and A values reported by Wu et al. are not far from the experimental ones due to the route followed for determining the fitting parameter.

Apart from this trouble, the analysis made by Wu et al. is unable to explain the actual origin of a relevant issue emerging in the comparison between the experimental g, A and 10Dq values of K MgF$_3$:Co$^{2+}$ and BaLiF$_3$:Co$^{2+}$ [5–8]. As the lattice parameter, $a$, of LiBaF$_3$ and K MgF$_3$ [9,10] are nearly identical (Table 1) it could be expected that the electronic properties due to the CoF$_6^{2-}$ complex in such lattices would be practically the same. In fact, within the traditional ligand field approach such properties are accounted for by considering only the isolated CoF$_6^{2-}$ complex. Therefore, according to this view the variations due to a host lattice change should be ascribed to the induced variations on the Co$^{2+}$–F$^-$ distance, $R$.

Available experimental values of g, A and 10Dq measured for Co$^{2+}$-doped BaLiF$_3$, K MgF$_3$ [5–8] and also K ZnF$_3$ [11] are gathered...
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Table 1

<table>
<thead>
<tr>
<th>Host lattice</th>
<th>r₀ (Å)</th>
<th>r (∆t)</th>
<th>A (MHz)</th>
<th>g</th>
<th>10Dq (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaLiF₃</td>
<td>1.998</td>
<td>2.030</td>
<td>284.1</td>
<td>4.316</td>
<td>9360</td>
</tr>
<tr>
<td>KMgF₃</td>
<td>1.993</td>
<td>2.045</td>
<td>312</td>
<td>4.371</td>
<td>8000</td>
</tr>
<tr>
<td>KZnF₃</td>
<td>2.027</td>
<td>2.075</td>
<td>324.6</td>
<td>4.376</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 1. For the sake of completeness the R values obtained by us for such systems by means of Density Functional Theory calculations are also collected in Table 1. The calculation procedure is the same previously employed for deriving the equilibrium metal-ligand distance for Ni²⁺ [12] and Mn²⁺ [4] impurities in BaLiF₃ and KMgF₃. The calculated values in Table 1 give R(KMgF₃:Co²⁺) – R(BaLiF₃:Co²⁺) = 1.5 pm a value quite similar to that obtained for the Ni²⁺ impurity [12]. Therefore, despite R is found to be practically the same for both lattices the experimental 10Dq value of BaLiF₃:Co²⁺ is however 17% higher than that for KMgF₃:Co²⁺ while A for the latter system is 10% higher than A = 284.1 MHz measured for BaLiF₃:Co²⁺. Moreover, the experimental g and A values in KMgF₃:Co²⁺ are closer to those measured for KZnF₃:Co²⁺ than to the corresponding figures in BaLiF₃:Co²⁺ despite R(KZnF₃:Co²⁺) – R(KMgF₃:Co²⁺) is found to be twice the value R(KMgF₃:Co²⁺) – R(BaLiF₃:Co²⁺). This analysis thus stresses that the significant differences between the experimental g, A and 10Dq values of KMgF₃:Co²⁺ and BaLiF₃:Co²⁺ can hardly be understood on the basis of a different Co²⁺–F⁻ distance in the CoF₄ complex embedded in the two host lattices.

This situation, though certainly surprising, follows however the same pattern already observed [4,12] in the comparison of spin Hamiltonian parameters and 10Dq for Ni²⁺ and Mn²⁺ impurities in BaLiF₃ and KMgF₃. It has been pointed out that although active electrons of a transition metal impurity, M, embedded in an insulating lattice are usually localized in the Mnₓ unit formed with the ligands, this complex is never isolated but subject to the electrostatic potential, V₀(r), due to all ions lying outside. As a salient feature the shape of V₀(r) plays a key role for comparing the properties of the same complex embedded in two lattices which are not isomorphic. While in a normal perovskite V₀(r) is essentially flat in the complex region this is no longer true in the case of an inverted perovskite where V₀(r) raises the energy of the anti-bonding e_x(3z²–r²); x²–y²) orbitals and ligand 2σ levels. This gives rise to a supplementary increase of 10Dq and also the covalency, a fact which lessens the crucial contribution of the core polarization to A. Moreover, if on passing from KMgF₃:Co²⁺ to BaLiF₃:Co²⁺ V₀(r) induces an additional increase of covalency and 10Dq this would give rise to a decrement of the gyromagnetic factor, g [13]. This fact is thus again in qualitative agreement with g values collected in Table 1.

The present analysis thus supports that the anomalous changes experienced by magnetic and optical parameters on passing from KMgF₃:M²⁺ to BaLiF₃:M²⁺ (M = Ni, Mn, Co) all obey to the same cause: the different shape of V₀(r) in the normal and inverted perovskite structures whose origin has previously been discussed [4,12]. Although the work of Ref.[12] is quoted in the paper by Wu et al., these authors appear not to have taken its main conclusion into consideration.

References